

CLAIMS

What is claimed is:

1. A curable, water-based coating composition comprising the reaction product of:
  - 5 (A) a water-dispersible cross-linking agent; and
  - (B) a water-based copolymer prepared by free-radical polymerization and comprising the reaction product of;
    - (I) a first block comprising the reaction product of;
      - (a) a plurality of ethylenically unsaturated monomers
      - 10 wherein at least one monomer of said plurality includes a functional group suitable for reaction with said cross-linking agent (A), and
      - (b) a vinylaromatic hydrocarbon monomer; and
    - (II) a second block comprising the reaction product of;
      - (a) a non-functional, ethylenically unsaturated monomer.
- 15 2. A coating composition as set forth in claim 1 wherein said functional group suitable for reaction with said cross-linking agent (A) is selected from the group consisting of carbonate functional groups, hydroxyl functional groups, and mixtures thereof.
3. A coating composition as set forth in claim 1 wherein said functional
- 20 group suitable for reaction with said cross-linking agent (A) is a carbonate functional group.
4. A coating composition as set forth in claim 3 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) comprises a first and second

ethylenically unsaturated monomer wherein said second ethylenically unsaturated monomer is suitable for reaction with said cross-linking agent (A).

5. A coating composition as set forth in claim 4 wherein said first ethylenically unsaturated monomer is acrylic acid.

5 6. A coating composition as set forth in claim 4 wherein said second ethylenically unsaturated monomer that is suitable for reaction with said cross-linking agent (A) is selected from the group consisting of carbonate-modified glycidyl acrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof.

7. A coating composition as set forth in claim 4 wherein said second  
10 ethylenically unsaturated monomer is carbonate-modified glycidyl methacrylate.

8. A coating composition as set forth in claim 4 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) further comprises methyl methacrylate as a third ethylenically unsaturated monomer.

9. A coating composition as set forth in claim 4 wherein said first  
15 ethylenically unsaturated monomer is selected from the group consisting of alkyl acrylic acids, and said second ethylenically unsaturated monomer is selected from the group consisting of cycloaliphatic acrylates, cycloaliphatic methacrylates, and mixtures thereof, wherein each of said first and second ethylenically unsaturated monomers include up to 20 carbon atoms in the alkyl radical.

20 10. A coating composition as set forth in claim 9 wherein the weight ratio of said first ethylenically unsaturated monomer to said second ethylenically unsaturated monomer is from 1 : 0.5 to 1 : 5.

11. A coating composition as set forth in claim 3 wherein said carbonate functional group suitable for reaction with said cross-linking agent (A) is modified into a carbamate functional group.

12. A coating composition as set forth in claim 11 further comprising the  
5 reaction product of an ammonia-containing compound reactive with said monomer of said plurality for modifying said carbonate functional group into said carbamate functional group.

13. A coating composition as set forth in claim 12 wherein said ammonia-containing compound is selected from the group consisting of ammonia, ammonium  
10 hydroxide, and mixtures thereof.

14. A coating composition as set forth in claim 11 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) comprises a first and second ethylenically unsaturated monomer wherein said second ethylenically unsaturated monomer is suitable for reaction with said cross-linking agent (A).

15. A coating composition as set forth in claim 14 wherein said first ethylenically unsaturated monomer is acrylic acid.

16. A coating composition as set forth in claim 14 wherein said second ethylenically unsaturated monomer that is suitable for reaction with said cross-linking agent (A) is selected from the group consisting of carbonate-modified glycidyl  
20 acrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof.

17. A coating composition as set forth in claim 14 wherein said second ethylenically unsaturated monomer is carbonate-modified glycidyl methacrylate.

18. A coating composition as set forth in claim 14 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) further comprises methyl methacrylate as a third ethylenically unsaturated monomer.

19. A coating composition as set forth in claim 14 wherein said first  
5 ethylenically unsaturated monomer is selected from the group consisting of alkyl acrylic acids, and said second ethylenically unsaturated monomer is selected from the group consisting of cycloaliphatic acrylates, cycloaliphatic methacrylates, and mixtures thereof, wherein each of said first and second ethylenically unsaturated monomers include up to 20 carbon atoms in the alkyl radical.

10 20. A coating composition as set forth in claim 11 wherein the weight ratio of said first ethylenically unsaturated monomer to said second ethylenically unsaturated monomer is from 1 : 0.5 to 1 : 5.

21. A coating composition as set forth in claim 1 wherein said functional  
15 group suitable for reaction with said cross-linking agent (A) is a hydroxyl functional group.

22. A coating composition as set forth in claim 21 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) comprises a first and second ethylenically unsaturated monomer wherein said second ethylenically unsaturated monomer is suitable for reaction with said cross-linking agent (A).

20 23. A coating composition as set forth in claim 22 wherein said first ethylenically unsaturated monomer is acrylic acid.

24. A coating composition as set forth in claim 22 wherein said second ethylenically unsaturated monomer is selected from the group consisting of

hydroxymethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxymethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, and mixtures thereof.

25. A coating composition as set forth in claim 22 wherein said second  
5 ethylenically unsaturated monomer is hydroxyethyl methacrylate.

26. A coating composition as set forth in claim 22 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) further comprises methyl methacrylate as a third ethylenically unsaturated monomer.

27. A coating composition as set forth in claim 22 wherein said first  
10 ethylenically unsaturated monomer is selected from the group consisting of alkyl acrylic acids, and said second ethylenically unsaturated monomer is selected from the group consisting of aliphatic acrylates, aliphatic methacrylates, and mixtures thereof, wherein each of said first and second ethylenically unsaturated monomers include up to 20 carbon atoms in the alkyl radical.

28. A coating composition as set forth in claim 27 wherein the weight ratio  
15 of said first ethylenically unsaturated monomer to said second ethylenically unsaturated monomer is from 1 : 0.5 to 1 : 5.

29. A coating composition as set forth in claim 1 wherein said plurality of ethylenically unsaturated monomers (B)(I)(a) are selected from the group of  
20 compounds consisting of aliphatic acrylates, aliphatic methacrylates, cycloaliphatic acrylates, cycloaliphatic methacrylates, alkyl acrylic acids, and mixtures thereof, each of said compounds having up to 20 carbon atoms in the alkyl radical.

30. A coating composition as set forth in claim 29 wherein said aliphatic acrylates are selected from the group consisting of alkyl acrylates, hydroxyalkyl acrylates, and mixtures thereof.

31. A coating composition as set forth in claim 30 wherein said alkyl  
5 acrylates are selected from the group consisting of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, ethylhexyl acrylate, stearyl acrylate, lauryl acrylate, and mixtures thereof.

32. A coating composition as set forth in claim 30 wherein said  
hydroxyalkyl acrylates are of the general formula  $R-OC(O)C(H):CH_2$ , wherein R is an  
10 alkyl radical having from 1 to 6 carbon atoms and at least one hydroxyl group.

33. A coating composition as set forth in claim 30 wherein said  
hydroxyalkyl acrylates are selected from the group consisting of hydroxymethyl  
acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, and  
mixtures thereof.

34. A coating composition as set forth in claim 29 wherein said aliphatic  
15 methacrylates are selected from the group consisting of alkyl methacrylates, hydroxyalkyl methacrylates, and mixtures thereof.

35. A coating composition as set forth in claim 34 wherein said alkyl  
methacrylates are selected from the group consisting of methyl methacrylate, ethyl  
20 methacrylate, propyl methacrylate, butyl methacrylate, hexyl methacrylate, ethylhexyl methacrylate, stearyl methacrylate, lauryl methacrylate, and mixtures thereof.

36. A coating composition as set forth in claim 34 wherein said hydroxyalkyl methacrylates are of the general formula  $R-OC(O)C(CH_3):CH_2$ , wherein R is an alkyl radical having from 1 to 6 carbon atoms and at least one hydroxyl group.

37. A coating composition as set forth in claim 34 wherein said  
5 hydroxyalkyl methacrylates are selected from the group consisting of hydroxymethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, and mixtures thereof.

38. A coating composition as set forth in claim 29 wherein said  
10 cycloaliphatic acrylates are selected from the group consisting of cyclohexyl acrylate, glycidyl acrylate, carbonate-modified glycidyl acrylate, and mixtures thereof.

39. A coating composition as set forth in claim 29 wherein said cycloaliphatic methacrylates are selected from the group consisting of cyclohexyl methacrylate, glycidyl methacrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof.

40. A coating composition as set forth in claim 29 wherein said alkyl  
15 acrylic acids are selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, and mixtures thereof.

41. A coating composition as set forth in claim 1 wherein said first block  
20 (A)(I) is present in an amount from 5 to 15 parts by weight based on 100 parts by weight of said coating composition.

42. A coating composition as set forth in claim 1 wherein said second block (A)(II) is present in an amount from 20 to 50 parts by weight based on 100 parts by weight of said coating composition.

43. A coating composition as set forth in claim 1 wherein said first block  
5 (B)(I) further comprises the reaction product of a neutralizing agent.

44. A coating composition as set forth in claim 43 wherein said neutralizing agent is selected from the group consisting of dimethylethanolamine, amino methyl propanol, ammonia, and mixtures thereof.

45. A coating composition as set forth in claim 1 wherein said first block  
10 (B)(I) further comprises the reaction product of an initiator.

46. A coating composition as set forth in claim 45 wherein said initiator is selected from the group consisting of inorganic persulfates, dialkyl peroxides, hydroperoxides, peresters, and mixtures thereof.

47. A coating composition as set forth in claim 45 wherein the weight ratio  
15 of said initiator to said at least one vinylaromatic hydrocarbon monomer (A)(I)(b) is from 1 : 3 to 3 : 1.

48. A coating composition as set forth in claim 1 wherein said at least one vinylaromatic hydrocarbon monomer (B)(I)(b) is selected from the group consisting of  $\alpha$ -methylstyrene, diphenylethylene, dinaphthaleneethylene, and mixtures thereof.

49. A coating composition as set forth in claim 1 wherein said non-  
20 functional, ethylenically unsaturated monomer (B)(II)(a) is further defined as an alkyl compound having from 2 to 20 carbon atoms in the alkyl radical and having no functional groups suitable for reaction with said cross-linking agent (A).



50. A coating composition as set forth in claim 1 wherein said non-functional, ethylenically unsaturated monomer (B)(II)(a) is selected from the group consisting of styrene, methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, glycidyl acrylate, glycidyl methacrylate, and mixtures thereof.

51. A coating composition as set forth in claim 1 wherein said non-functional, ethylenically unsaturated monomer (B)(II)(a) is selected from the group consisting of styrene, butyl methacrylate, 2-ethylhexyl methacrylate, and mixtures thereof.

52. A coating composition as set forth in claim 1 further comprising the reaction product of an anionic surfactant.

53. A coating composition as set forth in claim 1 wherein said first block (A)(I) has a molecular weight of from 1,000 to 20,000.

54. A coating composition as set forth in claim 1 having a non-volatile content of from 20 to 60 percent non-volatile by weight.

55. A coating composition as set forth in claim 1 having an average particle size of less than or equal to 200 nm.

56. A coating composition as set forth in claim 1 wherein said copolymer (B) has a molecular weight of from 5,000 to 5,000,000.

57. A coating composition as set forth in claim 1 wherein said water-dispersible cross-linking agent (A) is present in an amount from 0.1 to 15 parts by weight based on 100 parts by weight of said coating composition.

58. A coating composition as set forth in claim 1 wherein said water-dispersible cross-linking agent (A) is selected from the group consisting of water-dispersible aminoplasts, water-dispersible polymers having an acrylamide group, water-dispersible polymers having a methylol or alkoxymethyl group, water-soluble  
5 C<sub>2</sub> to C<sub>20</sub> alkyl compounds having an amino functional group, and mixtures thereof.

59. A coating composition as set forth in claim 11 wherein said water-dispersible cross-linking agent (A) comprises a water-dispersible aminoplast reactive with said carbamate functional group.

60. A coating composition as set forth in claim 59 wherein said water-  
10 dispersible aminoplast comprises a melamine formaldehyde resin having a methylol group, an alkoxymethyl group, or both, which are reactive with said carbamate functional group.

61. A coating composition as set forth in claim 21 wherein said water-dispersible cross-linking agent (A) comprises a water-dispersible aminoplast reactive  
15 with said hydroxyl functional group.

62. A coating composition as set forth in claim 61 wherein said water-dispersible aminoplast comprises a melamine formaldehyde resin having a methylol group, an alkoxymethyl group, or both, which are reactive with said hydroxyl functional group.

20 63. A coating composition as set forth in claim 3 wherein said water-dispersible cross-linking agent (A) comprises a water-soluble C<sub>2</sub> to C<sub>20</sub> alkyl compound having an amino functional group reactive with said carbonate functional group.

64. A coating composition as set forth in claim 63 wherein said water-soluble C<sub>2</sub> to C<sub>20</sub> alkyl compound having an amino functional group is selected from the group consisting of hexamethylenediamine, triaminononane, and mixtures thereof.

65. A coating composition as set forth in claim 1 wherein said water-  
5 dispersible cross-linking agent (A) comprises a melamine formaldehyde resin having a methylol group, an alkoxymethyl group, or both, which are reactive with said functional group.

66. A coating composition as set forth in claim 1 wherein said water-  
10 dispersible cross-linking agent (A) comprises a water-soluble C<sub>2</sub> to C<sub>20</sub> alkyl compound having an amino functional group.

67. A coating composition as set forth in claim 1 wherein said water-based copolymer (B) further comprises the reaction product of a third block, said third block comprising said at least one monomer of said plurality including said functional group suitable for reaction with said cross-linking agent (A).

68. A curable, water-based coating composition comprising the reaction product of:

- (A) a water-dispersible cross-linking agent; and
- 5 (B) a water-based copolymer prepared by free-radical polymerization and comprising the reaction product of;
  - (I) a first block comprising the reaction product of;
    - (a) an alkyl acrylic acid,
    - (b) an ethylenically unsaturated monomer including a
    - 10 functional group suitable for reaction with said cross-linking agent, and
    - (c) a vinylaromatic hydrocarbon monomer; and
  - (II) a second block comprising the reaction product of;
    - (a) a non-functional, ethylenically unsaturated monomer.

69. A coating composition as set forth in claim 68 wherein said functional  
15 group suitable for reaction with said cross-linking agent (A) is a carbonate functional group.

70. A coating composition as set forth in claim 69 wherein said carbonate functional group is modified into a carbamate functional group.

71. A coating composition as set forth in claim 70 further comprising the  
20 reaction product of an ammonia-containing compound reactive with said ethylenically unsaturated monomer for modifying said carbonate functional group into said carbamate functional group.

72. A coating composition as set forth in claim 68 wherein said functional group suitable for reaction with said cross-linking agent (A) is a hydroxyl functional group.

73. A coating composition as set forth in claim 69 wherein said water-  
5 dispersible cross-linking agent (A) is a water-dispersible C<sub>2</sub> to C<sub>20</sub> alkyl compound having an amino functional group reactive with said carbonate functional group.

74. A coating composition as set forth in claim 70 wherein said water-dispersible cross-linking agent (A) is a water-dispersible aminoplast reactive with said carbamate functional group.

10 75. A coating composition as set forth in claim 72 wherein said water-dispersible cross-linking agent (A) comprises a water-dispersible aminoplast reactive with said hydroxyl functional group.

76. A coating composition as set forth in claim 75 wherein said water-dispersible aminoplast comprises a melamine formaldehyde resin having a methylol  
15 group, an alkoxymethyl group, or both, which are reactive with said hydroxyl functional group.

77. A curable, water-based coating composition comprising the reaction product of:

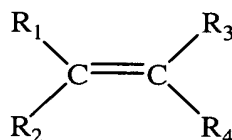
(A) a water-dispersible cross-linking agent; and

5 (B) a water-based copolymer prepared by free-radical polymerization and comprising the reaction product of;

(I) a first block comprising the reaction product of;

(a) a plurality of ethylenically unsaturated monomers wherein at least one monomer of said plurality includes a functional group suitable for  
10 reaction with said cross-linking agent (A), and

(b) at least one ethylenically unsaturated monomer different than said plurality of ethylenically unsaturated monomers (A)(I)(a) and of the general formula



15 wherein the radicals each independently of one another are hydrogen atoms or substituted or unsubstituted alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl or arylcycloalkyl radicals, with the proviso that at least two of the variables R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are substituted or unsubstituted aryl, arylalkyl or arylcycloalkyl radicals, especially substituted or unsubstituted aryl  
20 radicals; and

[illegible]

78. A layered-paint system applied wet-on-wet-on-wet onto a substrate, said layered-paint system comprising:

a first layer applied onto the substrate, said first layer comprising the reaction  
5 product of:

(A) a water-dispersible cross-linking agent; and

(B) a water-based copolymer prepared by free-radical polymerization and comprising the reaction product of;

(I) a first block comprising the reaction product of;

10 (a) a plurality of ethylenically unsaturated monomers wherein at least one monomer of said plurality includes a functional group suitable for reaction with said cross-linking agent (A), and

(b) a vinylaromatic hydrocarbon monomer; and

(II) a second block comprising the reaction product of;

15 (a) a non-functional, ethylenically unsaturated monomer;

a second layer applied onto said first layer, said second layer comprising a colored basecoat composition compatible with said first layer; and

a third layer applied onto said second layer, said third layer comprising a  
20 clearcoat composition compatible with said second layer.



79. A method of preparing a curable, water-based coating composition, said method comprising the steps of:

- (A) providing a water-dispersible cross-linking agent;
- 5 (B) forming a first block of a water-based copolymer wherein the first block includes a functional group suitable for reaction with the cross-linking agent;
- (C) polymerizing a second block, that includes a non-functional, ethylenically unsaturated monomer, with the first block to establish the water-based copolymer; and
- 10 (D) combining the water-based copolymer with the water-dispersible cross-linking agent that is reactive with the functional group of the copolymer to prepare the water-based coating composition.

80. A method as set forth in claim 79 wherein the steps of (B) and (C) are conducted at a temperature between 50°C and 100°C.

15 81. A method as set forth in claim 80 wherein the step of (B) forming the first block is further defined as polymerizing;

(a) a plurality of ethylenically unsaturated monomers wherein at least one monomer of the plurality includes the functional group; and

(b) a vinylaromatic hydrocarbon monomer;

20 to form the first block of the water-based copolymer.

82. A method as set forth in claim 81 wherein the step of polymerizing the plurality of ethylenically unsaturated monomers and the vinylaromatic hydrocarbon monomer is conducted over time from 1 to 8 hours.

83. A method as set forth in claim 81 wherein the plurality of ethylenically unsaturated monomers are selected from the group of compounds consisting of aliphatic acrylates, aliphatic methacrylates, cycloaliphatic acrylates, cycloaliphatic methacrylates, alkyl acrylic acids, and mixtures thereof, each of the compounds  
5 having up to 20 carbon atoms in the alkyl radical.

84. A method as set forth in claim 79 wherein the step of (B) forming the first block further comprises the step of adding a neutralizing agent selected from the group consisting of dimethylethanolamine, amino methyl propanol, ammonia, and mixtures thereof, to the plurality of ethylenically unsaturated monomers and the  
10 vinylaromatic hydrocarbon monomer to form the first block of the water-based copolymer.

85. A method as set forth in claim 79 wherein the step of (B) forming the first block further comprises the step of adding an initiator selected from the group consisting of inorganic persulfates, dialkyl peroxides, hydroperoxides, peresters, and  
15 mixtures thereof, to the plurality of ethylenically unsaturated monomers and the vinylaromatic hydrocarbon monomer to form the first block of the water-based copolymer.

86. A method as set forth in claim 79 wherein the vinylaromatic hydrocarbon monomer is selected from the group consisting of  $\alpha$ -methylstyrene,  
20 diphenylethylene, dinaphthaleneethylene, and mixtures thereof.

87. A method as set forth in claim 79 wherein the step of (C) polymerizing the second block, that includes the non-functional, ethylenically unsaturated monomer, with the first block is further defined as polymerizing a plurality of non-

functional, ethylenically unsaturated monomers with the first block to establish the water-based copolymer.

88. A method as set forth in claim 87 wherein the plurality of non-functional, ethylenically unsaturated monomers are selected from the group consisting of styrene, methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, glycidyl acrylate, glycidyl methacrylate, and mixtures thereof.

89. A method as set forth in claim 87 wherein the step of polymerizing the plurality of non-functional, ethylenically unsaturated monomers is conducted over time from 1 to 8 hours.

90. A method of preparing a cured film of a water-based coating composition, said method comprising the steps of:

- (A) providing a water-dispersible cross-linking agent;
- 5 (B) forming a first block of a water-based copolymer wherein the first block includes a functional group suitable for reaction with the cross-linking agent;
- (C) polymerizing a second block, that includes a non-functional, ethylenically unsaturated monomer, with the first block to establish the water-based copolymer;
- 10 (D) combining the water-based copolymer with the water-dispersible cross-linking agent that is reactive with the functional group of the copolymer to prepare the water-based coating composition;
- (E) applying the water-based coating composition to a substrate; and
- (F) curing the water-based coating composition to form the cured film.
- 15 91. A method as set forth in claim 90 wherein the step of (E) applying the water-based coating composition to the substrate is further defined as spraying the water-based coating composition on to the substrate.

- 92. A method as set forth in claim 90 wherein the step of (F) curing the water-based coating composition is further defined as reacting the functional group of
- 20 the first block with the water-dispersible cross-linking agent to prepare the cured film of the water-based coating composition.

93. A method as set forth in claim 92 wherein the step of reacting the functional group of the first block with the water-dispersible cross-linking agent is conducted at a temperature between 100°C and 175°C.

94. A method as set forth in claim 90 further comprising the step of  
5 applying a colored basecoat composition to the applied water-based coating composition prior to the step of (E) curing the water-based coating composition to form the cured film.

95. A method as set forth in claim 94 further comprising the step of  
10 applying a clearcoat composition to the applied colored basecoat composition prior to the step of (E) curing the water-based coating composition to form the cured film.

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